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Acidification of Rain in the Presence of SO2, H2O2, O3, and HNO3

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Acidification of Rain in the Presence of SO_2, H_2O_2, O_3, and HNO_3

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16. ABSTRACT

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ABSTRACT

ACIDIFICATION OF RAIN IN THE PRESENCE OF SO_2, H_2O_2, O_3 AND HNO_3

The production of acid sulfate and the accumulation of acid nitrate are calculated for falling raindrops using a physico-chemical model that accounts for the mass transfer of SO_2, H_2O_2, O_3, HNO_3, and CO_2. The acidification is postulated to occur through the absorption of free gaseous HNO_3 and the absorption and reaction of SO_2, H_2O_2, and O_3 to yield H_2SO_4. Investigated are the relative effectiveness of $H_2O_{2(aq)}$ and $O_{3(aq)}$ for oxidizing $SO_{2(aq)}$ to yield H^+ and SO_2^{2-}, and the role of $HNO_{3(g)}$ in acidifying raindrops and influencing SO_4^{2-} formation. Results indicate: that H_2O_2 is more effective than O_3, HNO_3 inhibits SO_4^{2-} formation due to O_3 oxidation, and in all cases, HNO_3 is important in acidifying rain.

INTRODUCTION

Odén[1] has performed an analysis of the data from the European wet deposition monitoring stations. He has observed these annual trends for each station since the mid-1950's: (a) pH has declined, (b) sulfate has increased, and (c) nitrate has increased. Presently, there is not a comparable long-term data base for precipitation in the United States. Likens and Bormann[2] have reported observing from 1964 to 1972 an upward trend in annual wet deposition of nitrate and hydrogen ion and a downward trend for sulfate. They also have noted similar trends of sulfate and nitrate at Geneva, NY and Ithaca, NY.

The projected growth in the energy sector of the economy in the Ohio River Valley should be expected to increase acid precipitation over downwind areas, especially the northeastern U.S. Relative to 1972 emissions in the valley, it is expected that by the year 2000 the emissions will change for SO_2 by a factor of -1 to 7% and for NO_x by a factor of 68 to 93%.[3] Thus, for the next 20 years, the role of NO_x in acidifying rain may likely become more important.

The important mechanisms by which rain is acidified are not yet established, but they include oxidation of SO_2 and NO_x in cloud droplets, nucleation of droplets from acid particles, and scavenging of free gaseous acids (HNO_3 and HCl) by droplets. Holt et al.[4] have used the technique of oxygen isotopy to investigate the pathway of SO_4^{2-} formation in raindrops; they concluded that oxidation in the droplet was always the prominant pathway. The principal oxidant is not known. However, using available reaction rate data, we have modeled the SO_4^{2-} formation rate for a sub-cloud event and found that ambient O_3 is much more effective than dissolved catalysts.[5] That work did not consider oxidation by H_2O_2. It is now known that $H_2O_{2(g)}$ may be present in the northeastern U.S. atmosphere in concentrations as high as 40 ppb.[6] Also, recent

experimental evidence on the reaction kinetics of $SO_{2(aq)}$ and $H_2O_{2(aq)}$ to yield H_2SO_4 has become available[7] that overcomes Dasgupta's[8] concerns of the previous work of Penkett et al.[9]

At this time, there is no experimental evidence that indicates the prominant pathway for NO_3^- formation in raindrops. Durham et al.[10] have recently modeled the effect of NO_2 (10 ppb) interacting with raindrops to yield NO, N_2O_3, N_2O_4 and HNO_2, followed by oxidation reactions to form HNO_3. That system was found to be unimportant. The only pathway yielding significant NO_3^- in raindrops was the absorption of free $HNO_{3(g)}$; free $HNO_{3(g)}$ is formed principally through the reaction of NO_2 and HO and often attains concentrations >10 ppb in the northeastern U.S.[11]

In this paper, we investigate: (a) the relative effectiveness of $H_2O_{2(aq)}$ and $O_{3(aq)}$ for oxidizing $SO_{2(aq)}$ to yield H^+ and SO_4^{2-}, and (b) the role of $HNO_{3(g)}$ in acidifying raindrops and influencing SO_4^{2-} formation. The important chemical behavior of rain in the presence of oxidants, HNO_3, and SO_2 was determined by simulations using the physical model and chemical reaction module that are described in the following sections.

PHYSICAL MODEL

Our physical model of a rain event, raindrops and mass transfer are described elsewhere[5,10]; thus, an abbreviated description is presented here.

The atmosphere has been divided into two regions, shown in Fig. 1. Raindrops are formed in the upper region in the presence of CO_2 and other compounds which establish the initial pH. The drops enter and fall through a stable polluted region at a constant velocity. In the polluted region are the trace gases CO_2, O_3, SO_2, HNO_3, and H_2O_2. As the drop falls, gases are absorbed, react and produce SO_4^{2-}, NO_3^- and other species. A raindrop is taken to be a uniform sphere composed of water and trace quantities of O_3, SO_2, CO_2, HNO_3, H_2O_2 and their products. Concentrations are assumed to be uniformly distributed at all times throughout the drop, (i.e., no concentration gradients in the drop). There is no coagulation or fragmentation of drops. Raindrop temperature is assumed to be in equilibrium with an isothermal atmosphere at 25°C (a choice dictated by the available chemical rate constant data). The raindrop size distribution is assumed to be independent of height and time and to be distributed according to the distribution of Best[12] truncated at a lower radius limit of 0.05 mm.

The rate, per unit fall distance, at which a gaseous species (e.g. O_3, HNO_3, H_2O_2, SO_2 and CO_2) crosses the gas-water interface of a drop of radius R is given by

$$\left.\frac{d[s]_\ell}{dz}\right|_{transfer} = \frac{0.3k_g}{Ru}\left([s]_g - H_s[s]_\ell\right)$$

The notation is presented in a section at the end of this chapter. The species, s, is assumed to be distributed uniformly through the drop. The mass transfer coefficient, k_g, is obtained from the Frössling correlation[13]. Values of u, the fall velocity, are obtained from a formula by Markowitz[14]. Henry's law constants, H_s, for the gaseous species are found in Table 1.

TABLE 1. HENRY'S LAW CONSTANTS

Species	H_s	Source of H_s values
CO_2	1.2	Perry and Chilton[15]
O_3	3.36	Perry and Chilton[15]
SO_2	0.0332	Hales and Sutter[16]
HNO_3	0.46E-6	Abel and Nuesser[17]; McKay[23]
H_2O_2	0.557E-6	Martin and Damschen[7]

CHEMICAL REACTION MODULE

The kinetic reactions used for this work are given in Table 2. Equations 1-6 are the reversible reactions for the CO_2-SO_2-HNO_3-H_2O system. The irreversible oxidation steps are given in equations 7 to 10. Reaction 10, H_2O_2 oxidation, is a compromise between the works of Martin and Damschen[7], Penkett et al.[9], and Hoffman and Edwards[18] and results in rates no more than twice or no less than one half the reported values in the pH range of interest.

TABLE 2. KINETIC MECHANISM OF CO_2-SO_2-HNO_3-O_3-H_2O_2-AQUEOUS PHASE SYSTEM USED FOR RAINDROPS*

1.	(H_2O)	$\underset{1.3E+11}{\overset{1.3E-3}{\rightleftharpoons}}$	$H^+ + OH^-$	Eigen et al.[19]
2.	$CO_2 + (H_2O)$	$\underset{4.92E+4}{\overset{2.4E-2}{\rightleftharpoons}}$	$HCO_3^- + H^+$	Himmelblau & Babb[20] (by extrapolation to 25°C)
3.	HCO_3^-	$\underset{1.4E+4}{\overset{1.0E-4}{\rightleftharpoons}}$	$CO_2 + OH^-$	Eigen et al.[19]
4.	$SO_2 + (H_2O)$	$\underset{2.0E+8}{\overset{3.4E+6}{\rightleftharpoons}}$	$H^+ + HSO_3^-$ (20°C)	Eigen et al.[19]
5.	HSO_3^-	$\underset{1.0E+11}{\overset{1.0E+4}{\rightleftharpoons}}$	$SO_3^{2-} + H^+$	Erickson & Yates[21] Erickson et al.[22]
6.	HNO_3	$\underset{1.0E+8}{\overset{2.2E+9}{\rightleftharpoons}}$	$H^+ + NO_3^-$	McKay[23]
7.	$O_3 + SO_2$	$\overset{5.9E+2}{\longrightarrow}$	$2H^+ + SO_4^{2-}$	Erickson et al.[22]
8.	$O_3 + SO_3^{2-}$	$\overset{2.2E+9}{\longrightarrow}$	SO_4^{2-}	Erickson et al.[22]
9.	$O_3 + HSO_3^-$	$\overset{3.1E+5}{\longrightarrow}$	$H^+ + SO_4^{2-}$	Erickson et al.[22]
10.	$H_2O_2 + HSO_3^- + H^+$	$\overset{7.3E+7}{\longrightarrow}$	$2H^+ + SO_4^{2-}$	Hoffman & Edwards[18] Penkett et al.[9] Martin & Damschen[7]

*Units are in liters, moles, seconds

MATHEMATICAL FORMULATION AND INTERPRETATION

The concentration (as a function of fall distance) of each chemical species within a drop of a given radius was obtained by numerically integrating the set of coupled non-linear differential equations derived from the kinetic and mass transport equations. This procedure was repeated for several different radii, and with the application of the Best[12] raindrop size distribution, simulated "samples" of rain water were computed. (A more detailed account of the mathematical formulation is found in Overton et al.[5] and Durham et al.[10].)

The "samples" of the simulated rainfall are: (1) "collected" sequentially, each one for several minutes, (2) isolated from ambient factors so there is no mass transfer with the atmosphere, (3) allowed to continue reacting. In addition, the SO_4^{2-} and pH values reported are those that would result if <u>all</u> the S(IV) were transformed to SO_4^{2-} (by, for example, a slow catalytic process over a long period of time due to storage in the collector or sample vials).

RESULTS AND DISCUSSIONS

The relative effectiveness of $H_2O_{2(aq)}$ and $O_{3(aq)}$ for oxidizing $SO_{2(aq)}$ and the role of HNO_3 are demonstrated by the results of simulations of 1000m, 10 mm/hr sequentially sampled rain events. These results have been divided into 5 cases. The first 3 cases are for rain events of 5-minute duration in which the air pollutant concentrations are assumed to remain constant as raindrops with an initial pH = 5.6 fall through the polluted zone. The 4th case is for an extented rain event in which gas pollutant concentrations are lowered during the event in response to washout by the rain. The 5th case compares the effect of pre-acidification (pH = 4) with the events for which the initial pH = 5.6.

Case I. Relative Effectiveness of H_2O_2 and O_3 on Acidification and SO_4^{2-} Formation

For a 5-minute period in a steady rain, we have calculated the pH and $[SO_4^{2-}]$ of drops with an initial pH = 5.6 that fall through a polluted zone (1000 m). The results are shown in Fig. 2 for which $HNO_{3(g)}$ is absent, $[SO_{2(g)}]$ = 10 ppb, and H_2O_2 (0-10 ppb) and O_3 (0-50 ppb) are variable. As can be seen in the slight negative slopes of the isolines, the relative effectiveness of H_2O_2 to O_3 is about 12 (ppb/ppb) for lowering pH and for forming SO_4^{2-} for the conditions listed in Fig. 2. For example, note the difference for $[H_2O_{2(g)}]$ = 10 ppb and $[O_{3(g)}]$ = 0 and 50 ppb: in the absence of O_3 the pH is 4.22, but when O_3 is increased to 50 ppb, the pH becomes 4.20. That is, 10 ppb of H_2O_2 drops the pH by 0.4 from 4.62 (at $[H_2O_2] = [O_3] = 0$) to 4.22, but an additional 50 ppb O_3 results only in a drop in pH by 0.02 from 4.22 to 4.20.

In the presence of $HNO_{3(g)}$ (not shown here), the relative effectiveness of H_2O_2 to O_3 increases. That is because H^+ inhibits the O_3 oxidation of dissolved SO_2 species, but not the H_2O_2 oxidation. In the absence and in the presence of $HNO_{3(g)}$, H_2O_2 is a more effective oxidizer than O_3.

Case II. Relative Effectiveness of HNO_3 and SO_2 on Acidification and SO_4^{2-} Formation

Two sub-cases, $[H_2O_{2(g)}]$ = 0 and 10 ppb, are considered in order to compare the relative effectiveness of HNO_3 and SO_2 in the presence of $[O_{3(g)}]$ = 50 ppb. The calculated pH, $[SO_4^{2-}]$, and $[NO_3^-]/[SO_4^{2-}]$ isopleths for a 5-minute rain sample are shown in Fig. 3 for $[H_2O_2]$ = 0. This system has been discussed in detail elsewhere[10]. The small (<-1.) negative slope of the pH isolines demonstrates the dominance of $HNO_{3(g)}$ in controlling the acidity of this system. Also, $HNO_{3(g)}$ is effective in suppressing $[SO_4^{2-}]$ formation due to O_3 oxidation. For example, at $[SO_{2(g)}]$ = 15 ppb, note that as $[HNO_{3(g)}]$ ranges from 0 to 10 ppb, $[SO_4^{2-}]$ falls from 17.5 μM to less than 12.5 μM, and pH declines by about 0.3.

The isolines for this system change dramatically when $H_2O_{2(g)}$ is present at 10 ppb, as is shown in Fig. 4. The pH isolines become steeper, indicating stronger dependence on $[SO_{2(g)}]$, and are significantly displaced to lower values. The $[SO_4^{2-}]$ isolines are essentially vertical, indicating that the SO_4^{2-} formation due to H_2O_2 oxidation is strongly dependent on $[SO_{2(g)}]$ and only weakly dependent on $HNO_{3(g)}$. For HNO_3 to contribute over 50% to the acidification ($[NO_3^-]/[SO_4^{2-}] \geq 2$), then the $HNO_{3(g)}$ concentration must exceed that of SO_2 by a factor of ~1.3. For $[SO_{2(g)}] \leq [H_2O_2]$ = 10 ppb, the effectiveness of SO_2 is approximately 1.3 of that of $HNO_{3(g)}$ for acidifying rain; however, as $[SO_{2(g)}] > [H_2O_{2(g)}]$, the relative effectiveness of $[SO_{2(g)}]$ declines. If $[SO_{2(g)}] > 7.5$ ppb, then $[HNO_{3(g)}]$ must be >10 ppb in order for $HNO_{3(g)}$ to dominate the acidification.

The behavior of the systems considered in Case II demonstrates that for $[O_{3(g)}]$ = 50 ppb: (a) $HNO_{3(g)}$ in the absence of H_2O_2 is more effective than SO_2 in acidifying rain and may limit SO_4^{2-} formation, but (b) in the presence of $H_2O_{2(g)}$, $SO_{2(g)}$ is more effective and the SO_4^{2-} formation rate is weakly dependent on $HNO_{3(g)}$.

Case III. Relative Effectiveness of H_2O_2 and HNO_3 on Acidification and SO_4^{2-} Formation

Two sub-cases are shown here in order to compare the relative effectiveness of H_2O_2 and HNO_3 (for $[O_{3(g)}] = 50$ ppb) in the presence of $[SO_{2(g)}] = 10$ ppb (see Fig. 5) and $[SO_{2(g)}] = 20$ ppb (see Fig. 6). This case is analogous to Case II. The influence of reaction 10 is being demonstrated. In Case II, $[HSO_3^-]$ from reaction 10 was the variable and in Case III, it is $[H_2O_2]$. In Fig. 5, $[H_2O_2] \leq [SO_{2(g)}] = 10$ ppb, and H_2O_2 and HNO_3 have approximately equal effectiveness for acidification; note however that SO_4^{2-} formation is only weakly dependent on HNO_3 (as observed for Case II). In Fig. 6, $[H_2O_2] \leq 10$ ppb and $[SO_{2(g)}] = 20$ ppb; due to this increase in $[SO_{2(g)}] / [H_2O_{2(g)}]$, the $SO_{2(aq)}$ oxidation by $H_2O_{2(aq)}$ become more important and HNO_3 less important to the acidification. That is illustrated by the increase (less negative) in slope of the pH isolines and their shift to lower values as $[SO_{2(g)}]$ is increased from 10 to 20 ppb.

This case is analogous to Case II, and $H_2O_{2(g)}$ is more effective than $HNO_{3(g)}$ in acidifying rain.

Case IV. Extended Rain Event

Figures 7 and 8 illustrate the interplay between rain concentrations and ambient gas concentrations for simulated 10 mm/hr, 1000 m, 60 minute rain events. In Fig. 7, $[H_2O_2] = 0$, we note the rapid decrease of $[HNO_3]_g$ accompanied by an even more rapid decrease of rain water NO_3^-. On the other hand we observe a slight increase in SO_4^{2-} due to an increase in pH (gaseous O_3 and SO_2 decrease at a much slower rate than HNO_3). Fig. 8, initial $[H_2O_2]_g = 5$ ppb, shows the nitrogen species behaving the same as in the absence of H_2O_2 along with the expected decrease of H_2O_2 due to its removal by the rain. Again the pH increases; however, in contrast to the $[H_2O_2] = 0$ case, SO_4^{2-} is initially twice as much and decreases (42% in 60 minutes) as the event

progresses. This decrease is obviously due to the removal of H_2O_2 from the atmosphere; note that the SO_4^{2-} curve "follows" the ambient H_2O_2 curve.

As pointed out, the behavior of HNO_3 and NO_3^- is the same in both cases (Figures 7 and 8). For the kinetic mechanism used $[NO_3^-]$ depends only on the fall distance and $[HNO_3]_g$. This is due to the very low Henry's law constant (that results in negligible HNO_3 back pressure) and to the dissociation of HNO_3 (Eq. 6, Table 2) in such a way that most of the nitrogen is in the form of NO_3^- and is thus insensitive to pH for a given quantity of nitrogen compounds.

The ratio, $[NO_3^-]/[SO_4^{2-}]$, (not shown) decreases in both cases; however, due to the near constancy of SO_4^{2-} in the $[H_2O_2] = 0$ case, the ratio decreases more rapidly than in the case when H_2O_2 is present.

Case V. Effect of Preacidification

Raindrops may be acidified prior to entering the polluted zone. Here we assume that occurs and that the raindrops have an initial pH = 4 and $[SO_4^{2-}] = 50$ μM prior to entering the polluted zone. The effect on pH and SO_4^{2-} formation for select values of HNO_3, O_3 and H_2O_2 in the presence of $[SO_2]_g = 10$ ppb is illustrated in Table 3 where values of the change in pH and SO_4^{2-} with respect to their initial values are shown. From the table we note the following: (a) preacidification limits further changes in pH and (b) in the presence of H_2O_2, SO_4^{2-} production is independent of preacidification (preacidification does limit SO_4^{2-} production by O_3 oxidation). However we point out that, as the H_2O_2 oxidation rate is independent of pH, conclusion (a) would no doubt have to be modified somewhat for fall heights of >1000 m; since, unlike the O_3 oxidation step, H_2O_2 will continue to oxidize S(IV). A fact to note is that a change of pH from 4.6 to 3.6 requires ten times as much hydrogen ions as the change from 5.6 to 4.6 and thus roughly a fall distance 10 times as much as that for a 5.6 to 4.6 pH change. Since the mass transfer rate is limited the quantity of mass (S_2, O_3, H_2O_2, etc.) that can be absorbed to produce $[H^+]$ is also limited; thus, the effective results of preacidification with respect to pH has the appearance of quenching the reaction.

TABLE 3. EFFECT OF PREACIDIFICATION (SO_2 = 10 ppb)*

Ambient Concentration, ppb				ΔpH		ΔSO_4^{2-}, μM	
HNO_3	O_3	H_2O_2	Initial pH:	5.6	4.0	5.6	4.0
0	0	0		-1.0	0	12.	2.0
0	50	0		-1.1	-.05	14.	6.6
10	0	0		-1.4	-.2	6.4	1.6
10	50	0		-1.4	-.2	8.6	1.9
0	0	10		-1.4	-.2	30.	26.
0	50	10		-1.4	-.2	32.	27.
10	0	10		-1.6	-.3	29.	26.
10	50	10		-1.7	-.3	30.	27.

*Fall height = 1000m, rain rate = 10 mm/hr

CONCLUSIONS

As a result of this investigation of the effect of SO_2, H_2O_2, O_3 and HNO_3 on the production of acidity in rain we conclude that:

(1) In the absence and in the presence of HNO_3, H_2O_2 is a more effective oxidizer than O_3.

(2) HNO_3, in the absence of H_2O_2, is more effective than SO_2 in acidifying rain and may limit SO_4^{2-} formation.

(3) In the presence of H_2O_2, SO_2 may be more effective than HNO_3 in acidifying rain; in this case the SO_4^{2-} formation rate is weakly dependent on HNO_3.

(4) NO_3^- formation, for the chemical mechanism used, depends mainly on ambient HNO_3, fall distance and rain rate, but not on pH.

(5) Acidification prior to entering polluted zone inhibits the further production of acidity (based on pH) and SO_4^{2-} in the absence of H_2O_2.

Meaningful comparisons of our simulations to field data can not be made as the model is limited in its assumptions and in its description of rain events[5,10]. However, the chemistry module used in these simulations contains many of the important reactions expected to take place in rain water, and as such the simulations do increase our understanding of the important chemical reactions in acidifying rain.

NOTATION

H	Henry's law constant, dimensionless. Equilibrium ratio of gas phase concentration to liquid phase concentration of same species.
R	drop radius, mm
aq	aqueous
g	indicates gas phase
hr	hour
k_g	gas phase mass transfer coefficient, cm/sec
l	liter
m	meter
mm	millimeter
s	indicates a chemical species such as SO_2, HNO_3, H^+, HSO_3^-, etc.
u	fall velocity, m/sec
z	fall distance, meters
ℓ	indicates liquid phase
[]	molar concentration
μM	10^{-6} moles/liter

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FIGURE CAPTIONS

No.

1 Environmental model. The raindrops form above and fall through the polluted zone. In the polluted zone, they absorb reactive gases which produce SO_4^{2-} and NO_3^-.

2 The effect of ambient H_2O_2 and O_3 on pH and sulfate in rain. Plotted are isopleths of pH (————) and SO_4^{2-} (— — — micromoles/liter) for ambient values of H_2O_2 and O_3. The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.63, ambient $[SO_2]$ = 10 ppb, ambient $[HNO_3]$ = 0 ppb.

3 The effect of ambient SO_2 and HNO_3 on pH, sulfate and nitrate in rain. Plotted are isopleths of pH (·····), SO_4^{2-} (— — — micromoles/liter), and the ratio (NO_3^-/SO_4^{2-}) (————) for ambient values of SO_2 and HNO_3. The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.63, ambient $[O_3]$ = 50 ppb, ambient $[H_2O_2]$ = 0 ppb. The absorption of HNO_3 by the falling droplets lowers the pH and retards the formation of SO_4^{2-} due to liquid phase reaction between dissolved O_3 and SO_2 species.

4 The effect of ambient SO_2 and HNO_3 on pH, sulfate and nitrate in the presence of H_2O_2. Plotted are isopleths of pH (·····), SO_4^{2-} (— — — micromoles/liter), and the ratio (NO_3^-/SO_4^{2-}) (————) for ambient values of SO_2 and HNO_3. The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.63, ambient $[O_3]$ = 50 ppb, ambient $[H_2O_2]$ = 10 ppb. The absorption of HNO_3 by the falling droplets lowers the pH and slightly retards the formation of SO_4^{2-}.

5 The effect of ambient H_2O_2 and HNO_3 on pH, sulfate and nitrate in rain. Plotted are isopleths of pH (·····), SO_4^{2-} (— — — micromoles/liter), and the ratio (NO_3^-/SO_4^{2-}) (————). The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.63, ambient $[O_3]$ = 50 ppb, ambient $[SO_2]$ = 10 ppb.

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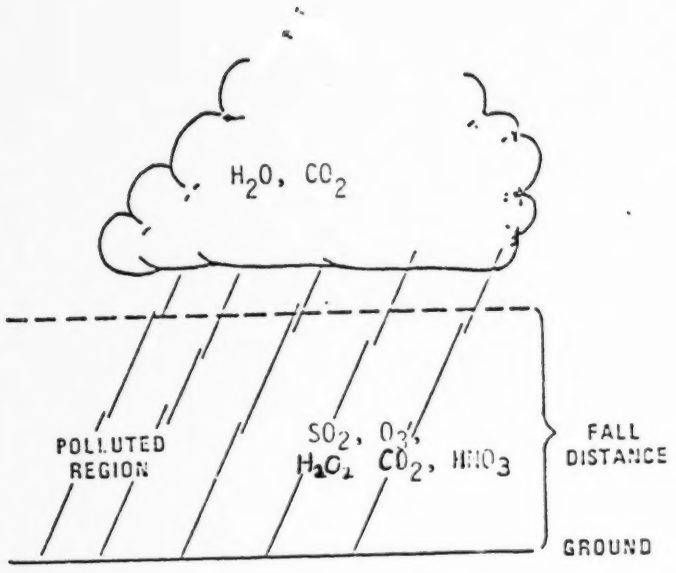

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Fig 2

4/4/81
2-5-81

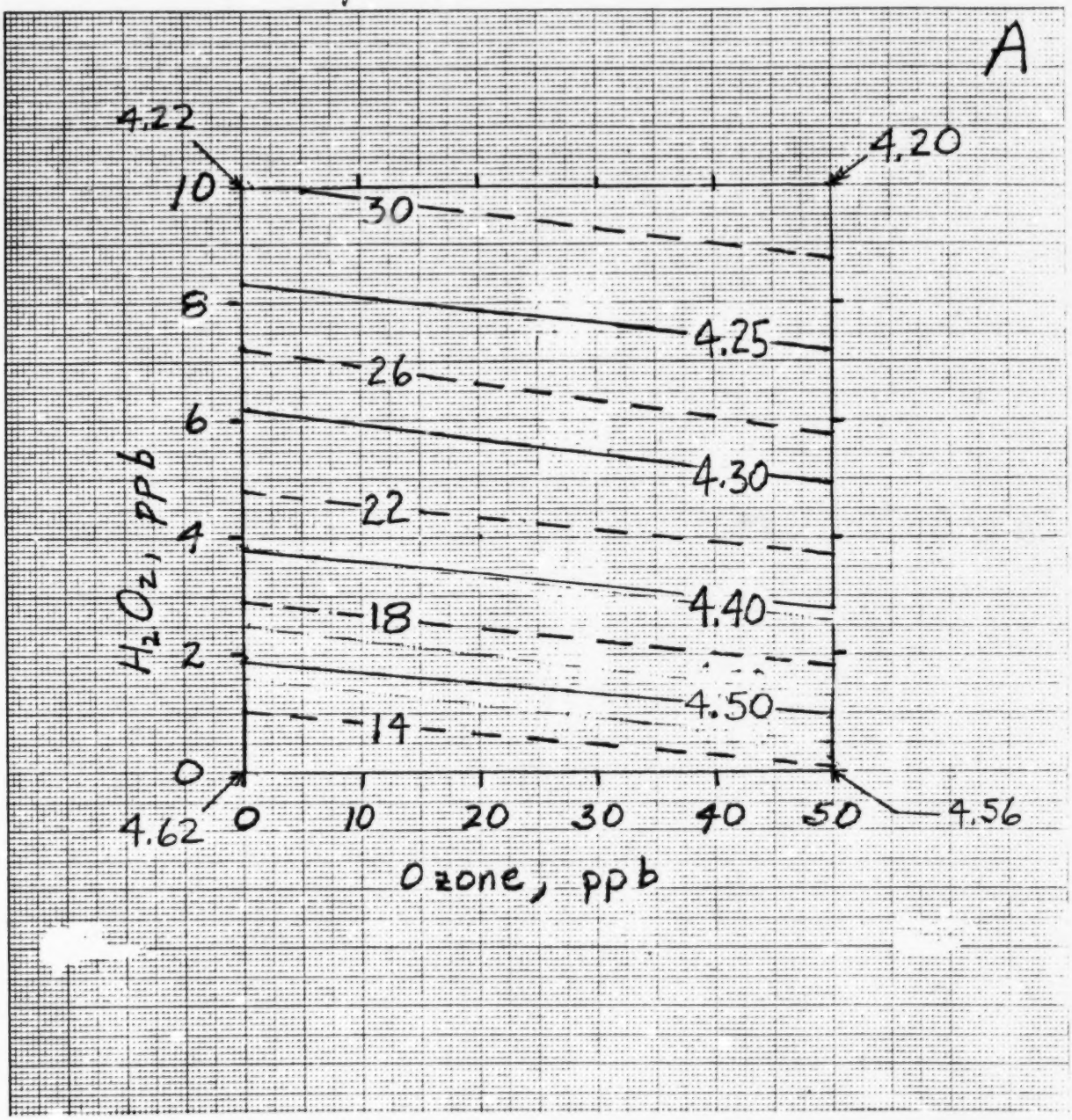

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Fig 3

4-5-81

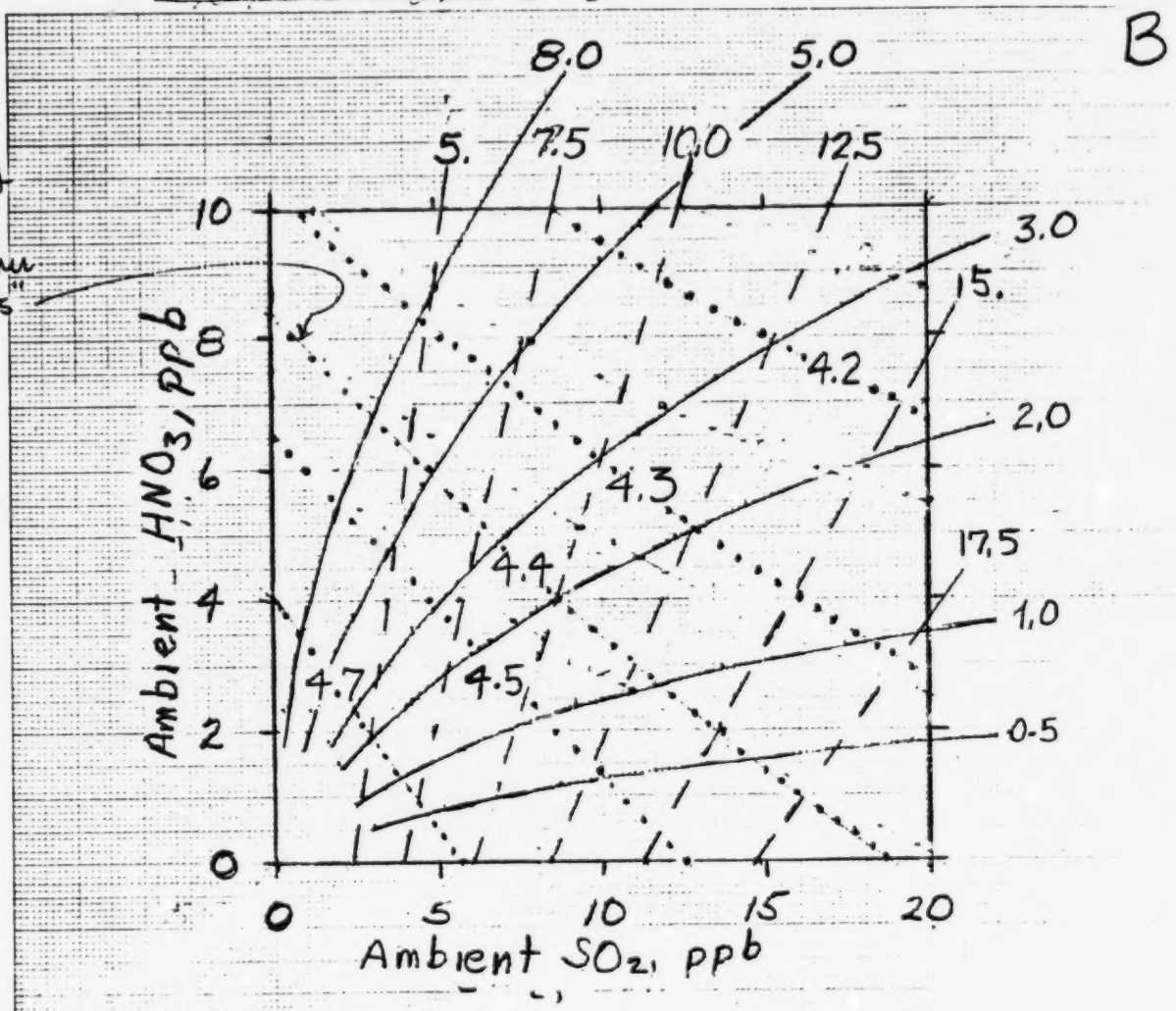

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Fig 4

$H_2O_2 = 10$ ~~$O_3 = 50$~~ $T = 10$ $\zeta = 1000$ 2-6-81 4-4-81

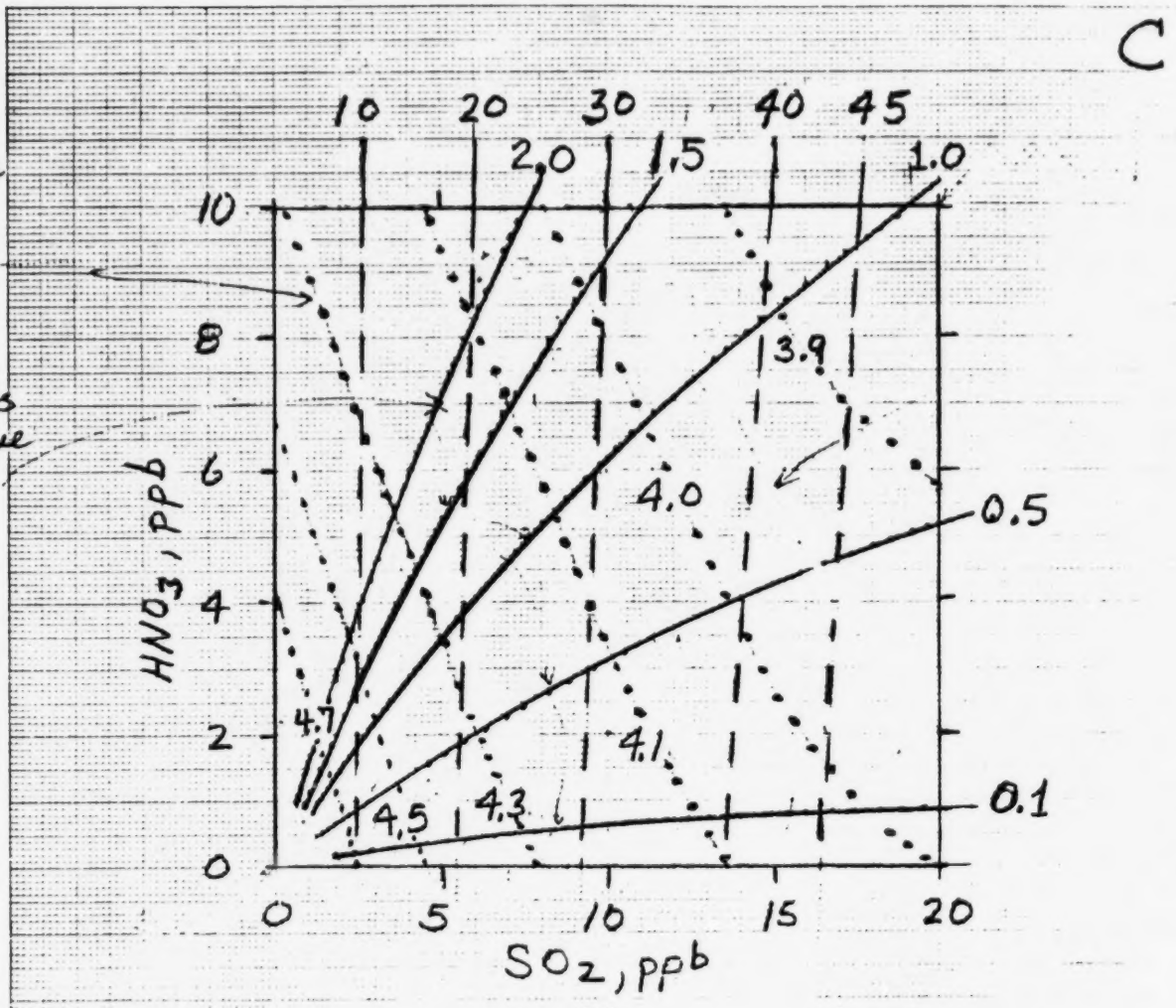

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Fig 5

4-9-81 1-36 81

E

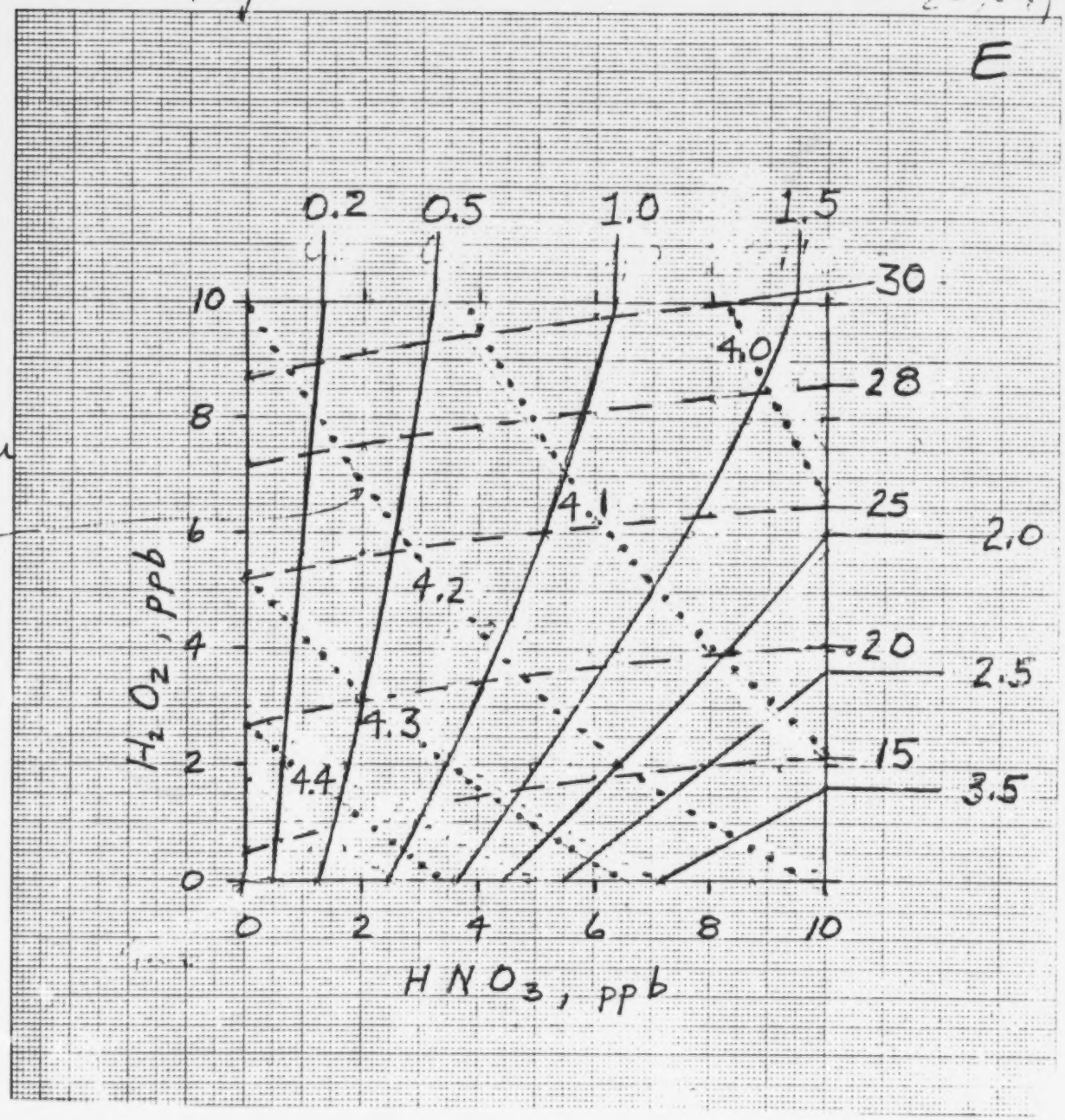

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Fig 6

4-5-81 1-30-81
-9-81

D

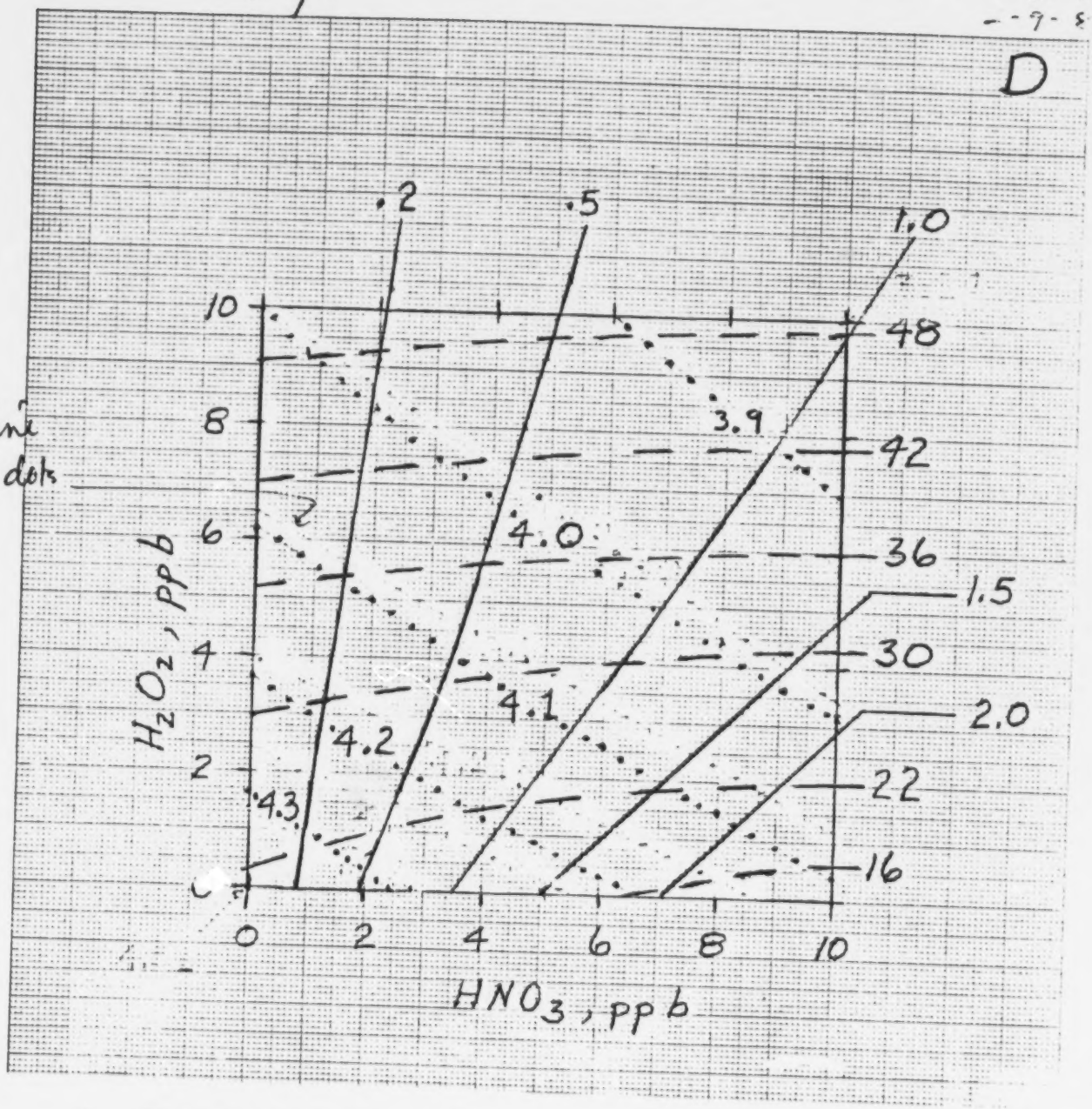

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Fig 7

4-4-81
2-481

F

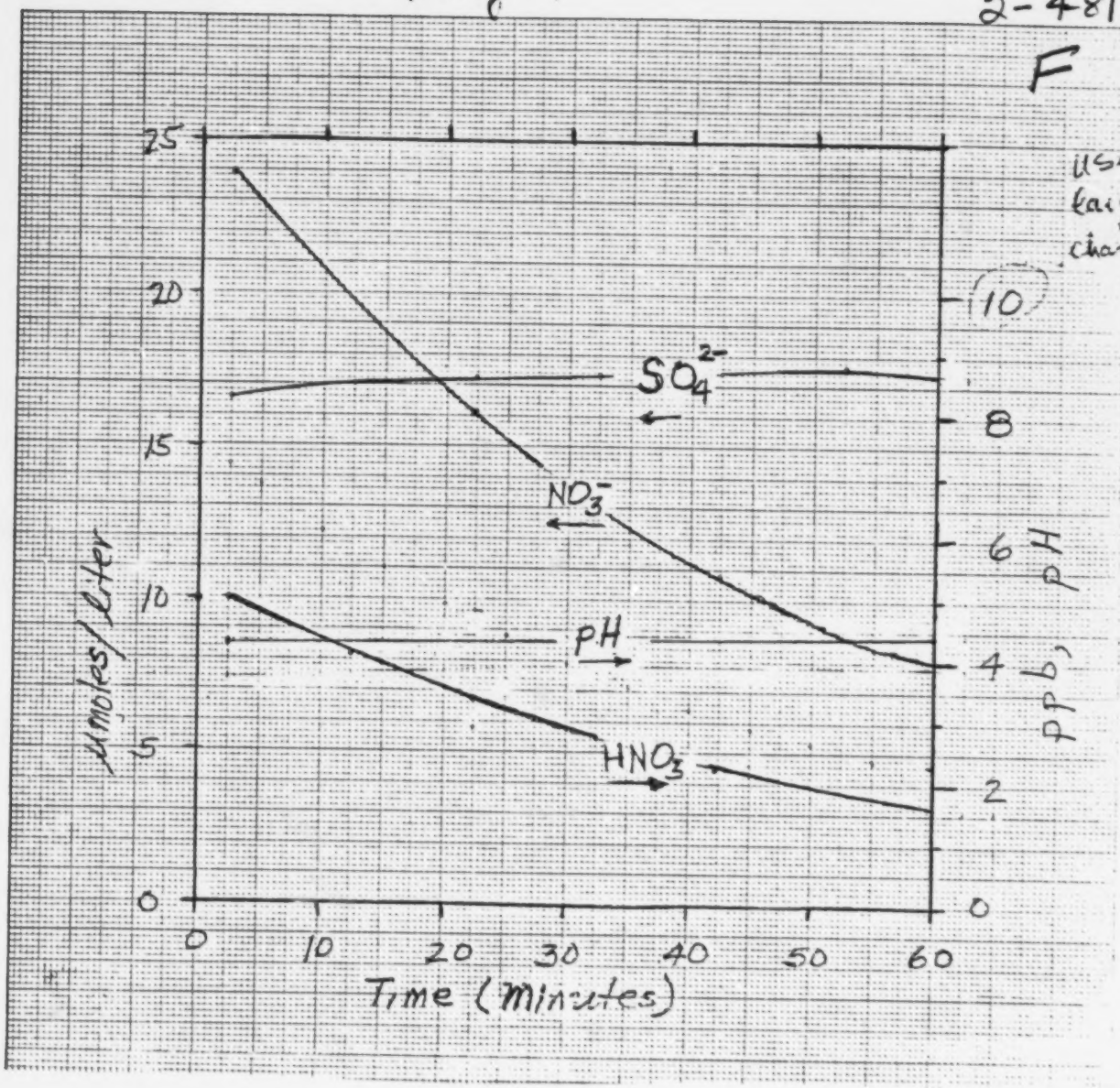

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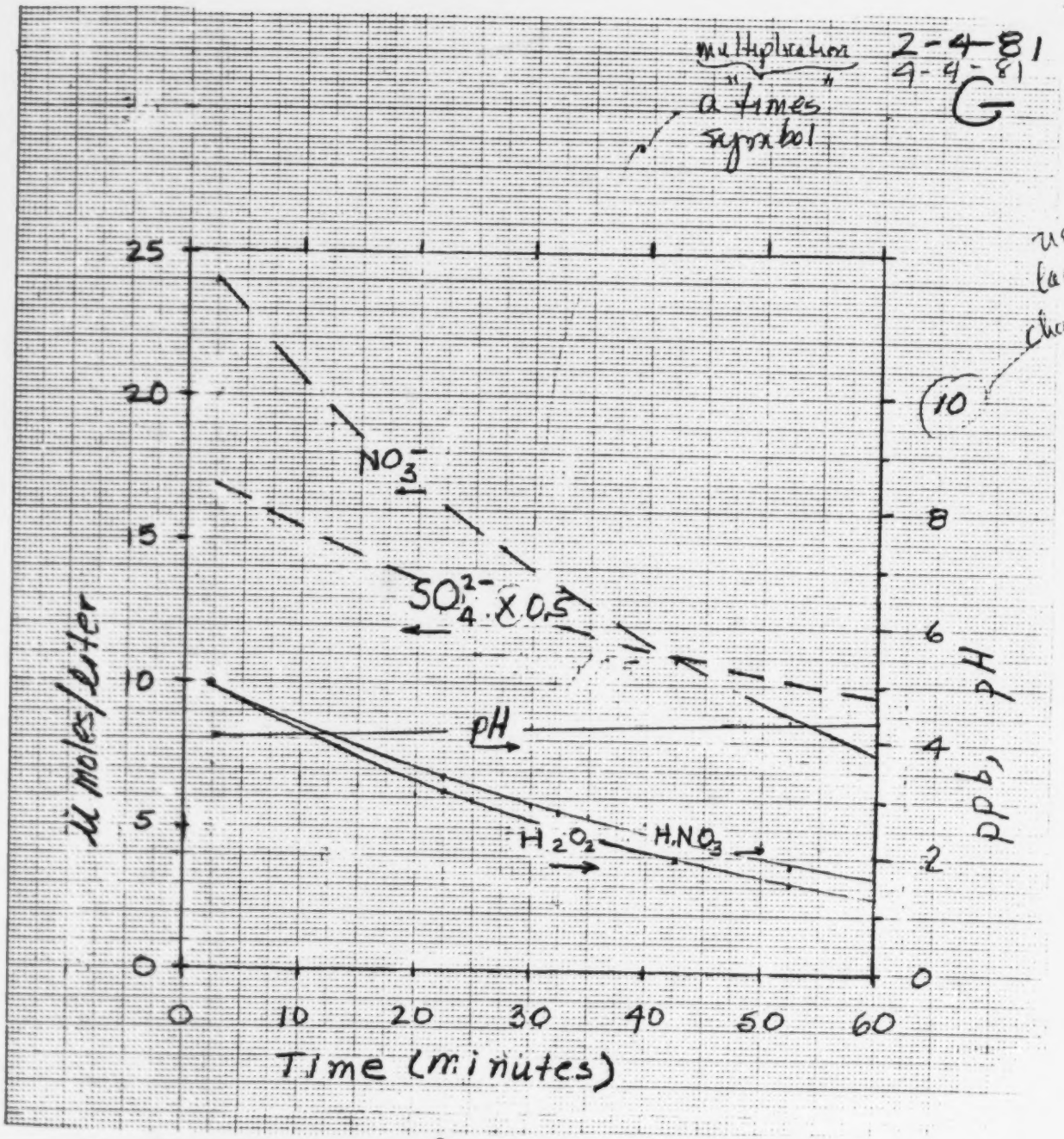
Fig. E



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